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(54) Title: **STABILIZED POLYMER COMPOSITION**

(57) Abstract: The present invention relates to an antioxidant composition comprising (a) 0.01-0.5% by weight of sterically hindered phenolic compound, (b) 0.01-0.5% by weight of phosphorous compound, and (c) 0.01-1% by weight of sulphurcontaining compound. Said antioxidant composition reduces degradation of plastic materials during processing and end-use and thus, increases the long term thermal stability of those plastic materials. Moreover, this invention relates to methods for producing a final polymeric article with an increased long term thermal stability and stabilization against ageing by radical decomposition processes and polymeric intermediate materials as well as polymeric articles comprising the inventive antioxidant composition.

WO 2004/033545 A1

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Stabilized polymer compositionTechnical field

- 5 The present invention relates to a stabilized polymer composition comprising a composition of antioxidants which reduces degradation of plastic materials during processing and end-use and thus, increases the long term thermal stability of those plastic materials. Moreover, this
- 10 invention relates to methods for producing a final polymeric article with an increased long term thermal stability and stabilization against ageing by radical decomposition processes and polymeric intermediate materials as well as polymeric articles comprising the inventive antioxidant
- 15 composition.

Background art

- Recent advances in the manufacturing and processing of
- 20 plastic polymers have led to the application of plastics in virtually every aspect of modern day life. However, polymeric compounds are prone to ageing under the effects of light, oxygen and heat. This results in a loss of strength, stiffness and flexibility, discolouration and scratching and
- 25 loss of gloss.

- Polymeric compounds, for example polyolefines like polyethylene and polypropylene undergo radical driven degradation processes especially during processing steps
- 30 which might include moulding, extrusion etc. However, degradation even proceeds during end-use by a radical mechanism under the influence of light, heat etc. and will finally destroy the polymer properties.

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It is well-known in the art that antioxidants and light stabilizers can prevent or at least reduce these effects. Several types of additives are added to polymers to protect them during processing and to achieve the desired end-use properties. Additives are generally divided in stabilizers and modifiers. Typical modifiers are antistatic- and anti-fogging agents, acid scavengers, blowing agents, cling agents, lubricants and resins, nucleating agents, slip- and anti-blocking agents as well as fillers, flame retardants, compatibilizers and crosslinkers.

Antioxidants traditionally and currently used comprise hindered phenolics, aromatic amines, organo-phosphites/phosphonites and thioethers. Neutralizers are often used to boost performance and diminish effects of residual polymer acidity.

Because of its sensitivity to oxidation, stabilization of polypropylene polymers against thermal oxidation is extremely important. Polypropylene polymers are probably the polymer most studied in this respect. At elevated temperatures and with excess of air, polypropylene polymers disintegrate to powdery oxidation products. This process is characterized by relatively well-defined and reproducible induction periods, commonly called oven lifetimes. Endpoints are easily detected even visually. The disintegration begins mostly at the etches and corners of the test species. It is often accompanied by yellow to brown discoloration.

An important aspect of process stabilization is that the degradation reaction products produced during processing can accelerate other types of a degradation later in the polymer life time, e.g. impede the light stability of the polymer.

For this reason, effective processing stability is essential in the production of durable plastic and articles.

Long term heat stability (LTHS) is an important property for many applications of polymers, especially polyolefines. Generally, long term thermal stability requirements are met by adding high concentrations of phenol antioxidants or combinations of phenols and thioethers to the polymer. Problems with such systems may be that tendency to yellowing increased by increased phenol concentrations or that the thioether may influence organoleptic properties in a negative way.

There are several approaches known in the prior art which address the problem of stabilization of polymers against radical decomposition which among others finally results in a loss of long term thermal stability of a polymer.

For example, US 6,015,854 teaches propylene-ethylene copolymers of high clarity and therefore incorporates clarifying agents into the copolymer mixture, however, the compositions disclosed therein may also contain stabilizers, antioxidants, lubricants, acid acceptors, synergists, anti-static agents, nucleating agents and additives which stabilize against radiation. To improve long term thermal stability, primary antioxidants of phenolic-type were added. Furthermore, it is stated that second type antioxidants like phosphites or hindered amines provide for an improved stability in melt flow and colour during the melt processing of the plastic material. The functions of all other primary and secondary antioxidants mentioned in the reference are well-known in the art. It is also disclosed that the synergistic enhance of the primary antioxidants can be achieved by including thioethers. However, this reference

focuses on clarity of the plastic material and consequently none of the properties measured in the examples is related to long term heat stability.

5 US 6,022,946 is directed to a method of deactivating catalyst residue in a polyolefin in a post-reactor vessel containing carbon monoxide. Claim 1 mentions the incorporation of an acid acceptor and at least one secondary antioxidant into the deactivated polyolefin polymer. This secondary antioxidant
10 may be an organic phosphite. Primary antioxidants including phenolic types are also mentioned with the main function to provide long term thermal stability. The synergistic enhance of this performance by including thioethers is also noted. Secondary antioxidants including phosphites are mentioned
15 which provide for improved colour and reduced melt flow breaking tendency. Again, this reference does not teach anything going beyond the general knowledge in the art according to which long term thermal stability can be controlled by the addition of a primary antioxidant and
20 optionally a synergistic thio-compound.

Though US 6,197,886 relates to polypropylene impact copolymers having improved mechanical properties, similar comments can be provided again.. There are polymeric
25 compositions disclosed which may contain antioxidants. Primary antioxidants, including phenolic types are mentioned with the main function to provide long term heat stability. The synergistic enhance of this performance by including thioethers is also mentioned. Furthermore, addition of
30 secondary antioxidants including phosphites with the focus on the improvement of the melt processing are disclosed as well. However, nothing can be taken from that reference which would enable the skilled artisan to achieve an improved long term thermal stability exceeding those already known in the art.

Furthermore, US 6,090,877 relates to a low smoke forming, acid neutralized propylene polymer composition comprising a propylene and an acid scavenging amount of mono potassium
5 citrate. Phenolics and phosphites are mentioned as possible antioxidants for polypropylene together with potassium citrate as an acid scavenger but this reference is quiet with regard to long term thermal stability of the propylene polymer compositions.

10

Another prior art reference (Zweifel, H., Stabilization of Polymeric Materials, Springer-Verlag, 1998, p. 76) reflects the general and well-established view in the art on the best mode to control long term thermal stability in polymers:

15

"In contrast to stabilization during processing, the presence of phosphites had not significant influence on long term thermal ageing of polyolefines".

20 Likewise, Schwartzzenbach et al., in Zweifel's, Plastic Additives Handbook, 5th edition, Hanser Publishers, 2001, p. 53 states:

25 "Phosphites do not contribute to long term thermal stability themselves. Long term thermal stability is only protected by the available phenol concentration. To improve long term thermal stability, thiosynergists as hydroperoxide decomposers in combination with a phenol are recommended."

30 Though, the necessary level of long term stability of a specific plastic material very much depends on the intended technical application thereof, there still exists a continued need for an improved control of this polymer property during processing steps and end use of the polymer. As discussed

above, the prior art teaching suggests to apply an antioxidant composition of a phenolic compound and a thiosynergist for hydroperoxide decomposition to the polymeric base material to reduce long term thermal ageing.

5

Therefore, the major focus to increase long term thermal stability of a polymer relied so far in the provision of improved phenolic-type and thioether antioxidants. That is to say, specific antioxidant compounds were developed which provide for example for a low volatility, high melting point, hydrolytic and thermal stability as well as the absence of unwanted side effects like having a colouring effect or an unclear toxicological profile which could jeopardize FDA and/or EU-SCF approvals. Most of those properties of the state of the art antioxidants are met by the unique structural features of these compounds, for example bulky residues of tert.-butyl substituted phenyl residues which provide for sterical hindrance to lower volatility in combination with a high molecular weight of those compounds.

20

In the state of art, the most obvious way to further increase long term thermal stability is generally seen in the use of higher amounts of those antioxidants. However, it is likewise obvious that simply increasing the antioxidant concentration in the polymer composition will most likely affect the properties of the final plastic material in a negative way. Therefore, it is highly desirable to be able to reduce long term thermal ageing with even less antioxidant compounds used in the polymer composition.

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Description of the invention

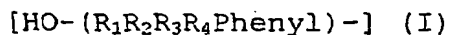
The inventors of the present application have addressed this issue by a different approach than those described above in

the prior art. The underlying problem of this invention is to be seen in the provision of polymers comprising specific antioxidant compositions which already allow to improve long term thermal stability of said polymeric material at very low concentrations of antioxidant compounds. Moreover, at the same time this stability towards thermal ageing should be further increased in view of long term thermal stabilities achieved so far by prior art approaches. Furthermore, such a composition of antioxidants should provide for a highly effective and versatile stabilization which is useful in a wide variety of applications. Likewise, this composition should be characterized by its superior thermal stability and low volatility, excellent atmospheric and in-polymer hydrolytic stability, outstanding protection against discoloration and degradation during processing, and excellent protection against long term polymer degradation.

In accordance with this objective, and other objectives that will be readily apparent to those skilled in the art upon reading this disclosure, it was surprisingly found that the specific combination of a phenolic compound together with a phosphite and a sulphur-containing compound substantially increase the long term heat stability of a polymer at unexpected low concentrations.

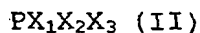
In accordance with the invention, it is provided a stabilized polymer composition comprising a polymer and an antioxidant composition for improving the long term heat stability of polymers, in particular polyolefins, said polymer composition comprising:

(a) 0,01% - 0,5% by weight of at least one sterically hindered phenolic compound, wherein said phenolic compound contains at least one phenolic moiety of general formula (I):



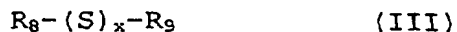
wherein R_1 , R_2 , R_3 or R_4 may be the same or different and at least one of R_1 , R_2 , R_3 or R_4 is selected from the group consisting of branched alkyl having 1 to 12 carbon atoms, preferably tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl, the others of R_1 , R_2 , R_3 or R_4 being H or lower alkyl having 1 to 6 carbon atoms;

(b) 0,01% - 0,5% by weight of at least one phosphorous compound, wherein said phosphorous compound contains at least one phosphorous compound moiety of general formula (II):



wherein X_1 may be R_5 or OR_5 , X_2 may be R_6 or OR_6 , X_3 may be R_7 or OR_7 and R_5 , R_6 or R_7 may be the same or different and at least one of R_5 , R_6 or R_7 is selected from the group consisting of C_1 - C_{25} alkyl group, aryl group or aralkyl group which may be substituted by lower alkyl having 1 to 6 carbon atoms, or two or any of R_5 , R_6 or R_7 may form a ring structure having 4 to 12 carbon atoms,

(c) 0,01% - 1% by weight of at least one sulphur-containing compound of general formula (III):



wherein $x = 1$ or 2 , and wherein R_8 and R_9 may be the same or different and are selected from the group consisting of C_{10} - C_{25} alkyl groups optionally being substituted with C_1 - C_{12} alkyl ester carboxylates, wherein said % by weight values are referred to the polymer composition.

In a preferred embodiment, the stabilized polymer composition comprises a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

5 (a) 0,02% - 0,2% by weight of said at least one sterically hindered phenolic compound,

(b) 0,03% - 0,2% by weight of said at least one phosphorous compound, and

10 (c) 0,05% - 0,6% by weight of said at least one sulphur-containing compound of general formula (III), wherein said % by weight values are referred to the polymer composition.

In a further preferred embodiment, the stabilized polymer composition comprises a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

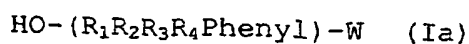
15 (a) 0,03% - 0,15% by weight of said at least one sterically hindered phenolic compound,

20 (b) 0,05% - 0,15% by weight of said at least one phosphorous compound, and

(c) 0,1% - 0,5% by weight of said at least one sulphur-containing compound of general formula (III), wherein said % by weight values are referred to the polymer composition.

25 When using the inventive antioxidant composition, further compounds selected from additives, fillers, minerals and lubricants can be compounded to the polyolefin for improving the processability and surface characteristics thereof.

30 The phenolic compound contains preferably at least one phenolic moiety of general formula (Ia):



wherein R_1 and R_4 being in the 2- and 6-position of the phenol residue may be the same or different and are selected from the group consisting of preferably branched C_1 to C_{12} alkyl, particularly tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl residues, R_2 and R_3 having the meaning as given before, and W is selected from C_1 to C_{12} alkyl, C_1 to C_{12} alkoxy, C_1 to C_{12} alkyl carboxylate or C_1 to C_{12} alkyl substituted by a further group of the formula HO-
10 ($R_1R_2R_3R_4$ Phenyl)-, wherein R_1 to R_4 have the meaning as indicated before.

In accordance with the present invention, it is particularly preferred that at least one of the following phenolic-type
15 antioxidant compounds is comprised by the inventive antioxidant compositions. These are the sterically hindered phenolic compounds:

- 2,6-Di-tert.-butyl-4-methyl phenol;
- Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-
20 hydroxyphenyl)-propionate;
- Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;
- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
- 25 - 2,2'-Thiodiethylene-bis-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- Calcium-(3,5-di-tert.-butyl-4-hydroxy benzyl monoethyl-phosphonate);
- 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-
30 isocyanurate;
- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl)butanoic acid)-glycolester;
- 4,4'-Thiobis (2-tert.-butyl-5-methylphenol);
- 2,2'-Methylene-bis(6-(1-methyl-cyclohexyl)para-cresol);

- N,N'-hexamethylene bis(3,5-di-tert. Butyl-4-hydroxy-hydrocinnamamide;
- 2,5,7,8-Tetramethyl-2(4',8',12'-trimethyltridecyl)chroman-6-ol;
- 5 - 2,2'-Ethylidenebis (4,6-di-tert.-butylphenol);
- 1,1,3-Tris(2-methyl-4-hydroxy-5-tert.-butylphenyl)butane;
- 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;
- 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro
- 10 (5,5)undecane;
- 1,6-Hexanediyl-bis(3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene-propanoate);
- 2,6-Di-tert.-butyl-4-nonylphenol;
- 15 - 3,5-Di-tert.-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris (2-hydroxyethyl)-s-triazine-2,4,6(1H,3H,5H)-trione;
- 4,4'-Butylidenebis(6-tert. Butyl-3-methylphenol);
- 2,2'-Methylene bis (4-methyl-6-tert.-butylphenol);
- 20 - 2,2-Bis(4-(2-(3,5-di-t-butyl-4-hydroxyhydrocinnamoyloxy))ethoxyphenyl))propane;
- Triethyleneglycole-bis-(3-tert.-butyl-4-hydroxy-5-methylphenyl) propionate;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, C₁₃-C₁₅-branched and linear alkyl esters;
- 25 - 6,6'-Di-tert.-butyl-2,2'-thiodi-p-cresol;
- Diethyl((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl)phosphonate;
- 4,6-Bis(octylthiomethyl)o-cresol;
- 30 - Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, C₇-C₉-branched and linear alkyl esters;
- 1,1,3-Tris[2-methyl-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-5-t-butylphenyl] butane; and

- a butylated reaction product of p-cresol and dicyclopentadiene.

Among those compounds, the following phenolic-type

- 5 antioxidant compounds are especially preferred to be included in the antioxidant composition according to the present invention:
- Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;
 - 10 - Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;
 - 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
 - 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-
 - 15 isocyanurate.
 - Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl)butanoic acid)-glycolester; and
 - 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro
 - 20 (5,5)undecane;

Furthermore, it is preferred that the phosphorous compound of the inventive antioxidant compositions contains a phosphite moiety of general formula bis(R₁₀)-pentaerythritol-

25 diphosphite, wherein R₁₀ is selected from C₁-C₂₅ alkyl group or aryl group which may be substituted by lower alkyl having 1 to 6 carbon atoms.

- In accordance with the present invention, it is also
- 30 preferred that at least one of the following phosphorous-type antioxidant compounds is comprised by the inventive antioxidant compositions. These are the phosphorous compounds:

- Tris (2,4-di-t-butylphenyl) phosphite;

- Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite
- Bis (2,4-di-t-butylphenyl)-pentaerythrityl-di-phosphite;
- Di-stearyl-pentaerythrityl-di-phosphite;
- 5 - Tris-nonylphenyl phosphite;
- Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
- 2,2'-Methylenebis (4,6-di-t-butylphenyl) octyl-phosphite;
- 1,1,3-Tris (2-methyl-4-ditridecyl phosphite-5-t-
- 10 butylphenyl) butane;
- 4,4'-Butylidenebis (3-methyl-6-t-butylphenyl-di-tridecyl) phosphite;
- Bis(2,4-dicumylphenyl)pentaerythritol diphosphite;
- Bis(2-methyl-4,6-bis(1,1-dimethylethyl)phenyl)phosphorous
- 15 acid ethylester;
- 2,2',2''-Nitrilo triethyl-tris(3,3',5,5'-tetra-t-butyl-1,1'-biphenyl-2,2'-diyl)phosphite);
- Phosphorous acid, cyclic butylethyl propandiol, 2,4,6-tri-t-butylphenyl ester;
- 20 - Bis (2,4,6-tri-t-butylphenyl)-pentaerythrityl-di-phosphite;
- 2,2'-Ethylidenebis (4,6-di-t-butylphenyl) fluorophosphonite
- 6- (3-tert-Butyl-4-hydroxy-5-methylphenyl) propoxy)-2,4,8,10-tetra-tert. butyldibenz (d,t) (1.3.2) dioxaphosphopin; and
- 25 - Tetrakis-(2,4-di-t-butyl-5-methyl-phenyl)-4,4'-biphenylen-di-phosphonite

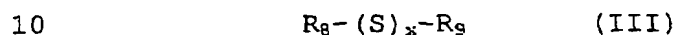
Among those compounds, the following phosphite/phosphonite-type antioxidant compounds are especially preferred to be

30 included in an antioxidant composition according to the present invention:

- -

- Tetrakis-(2,4-di-*t*-butylphenyl)-4,4'-biphenylen-di-phosphonite;
- Bis(2,6-di-*t*-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
- 5 - Di-stearyl-pentaerythrityl-di-phosphite; and
- Bis(2,4-dicumylphenyl)pentaerythritol diphosphite.

In accordance with the present invention, the sulphur-containing compound of general formula (III):



is selected from Di(C₁-C₂₀)alkyl-(S)_x-di-carboxylate wherein the carboxylic acid is selected from C₁ to C₁₀ alkyl carboxylic acids. Some of those preferred compounds are exemplified as follows:

- 15 - Di-stearyl-thio-di-propionate;
- Di-palmityl/stearyl-thio-di-propionate;
- Di-lauryl-thio-di-propionate;
- Di-tridecyl-thio-di-propionate;
- Di-myristyl-thio-di-propionate;
- 20 - Pentaerythritol octyl thiodipropionate;
- Lauryl-stearyl-thio-di-propionate;
- Di-octadecyl-disulphide;
- Di-tert-dodecyl-disulphide; and
- Pentaerythritol-tetrakis-(3-laurylthiopropionate);
- 25 wherein Di-stearyl-thio-di-propionate and Di-tert-dodecyl-disulphide are especially preferred.

In a particularly preferred embodiment, the inventive antioxidant composition is such that it comprises a mixture

30 of, as the sterically hindered phenolic compound, 1,3,5-Tris(4-*tert*.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione or Pentaerythrityl-tetrakis(3-(3',5'-di-*tert*.-Butyl-4-hydroxyphenyl)-propionate,

as the phosphite compound, bis(2,4-dicumylphenyl)pentaerythritol diphosphite; and, as the sulphur-containing compound, di-stearyl-thio-di-propionate. Moreover, the inventive antioxidant composition may

5 optionally further comprise metal deactivators and/or UV-stabilisers, wherein preferably said UV-stabilizers are sterically hindered amines.

It is another object of the present invention to provide a

10 polymeric material which comprises the above-described antioxidant composition and at least one polymer selected from the group consisting of polyolefines, polyethers, polyimides, polyamides and polyesters. If said at least one polymer comprises a polyolefin, it is preferred that the

15 polyolefin polymer is a homo- or co-polymer of polyethylene, polypropylene and polybutadiene.

In accordance with a further object, the present invention, provided for the use of the above-described antioxidant

20 composition to reduce degradation of a polymeric material by radical mechanisms during processing and end use of said polymeric material and preferably to increase the long term thermal stability of the polymeric material.

25 In yet another object of the present invention, there is provided a method for producing a final polymeric article with an increased long term thermal stability against ageing by radical degradation processes comprising the steps of:

- 30 (a) providing an unstabilised base polymer material;
- (b) adding to said base polymer material the inventive antioxidant composition;
- (c) converting the composition obtained in step (b) in a melt-forming process; and

(d) confectioning the polymeric material obtained in step (c).

This method may optionally include the further step
5 concerning the addition of other stabilisers and/or modifiers before the converting step.

The converting step typically includes injection moulding, blow moulding, rotational moulding and/or extrusion and the
10 confectioning step generally comprises cutting, lamination and/or welding.

Furthermore, it is still another object of the present invention to provide a polymeric article having a long term
15 ageing stability and being obtainable by one of the above-described methods for producing a final polymeric article.

Examples

In each of the following formulations of antioxidant
20 compositions, the thioether Di-stearyl-thio-di-propionate was used as the sulphur-containing compound (c) at a concentration of 3000 ppm. Furthermore, a polypropylene homopolymer in form of an unstabilised powder was selected to verify the effect of the inventive antioxidant compositions
25 on long term thermal stabilization. Beside the inventive antioxidant compositions, only 600 ppm Ca-stearate and partly 2000 ppm talc were further included into the polymer mixture as non-antioxidant additives where indicated.

30 The compounding steps were carried out for each formulation in a Prism extruder at the extruder condition of 210°C, 1 bar N₂.

Base polymer:

PP-homopolymer unstabilised powder mfr (230°C/2.16 kg) 3 g/10 min.

Non-antioxidant additives:

- 5 Ca-stearate (Calcium stearate SP, Faci, NO1), talc (Tital 10, Incemin AG, NO2),

Antioxidant additives:

(a) Phenolic-type compound (I)

- 10 - Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate (Irganox 1010 TM, Ciba Specialty Chemicals, AO-I-1),
- 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (Cyanox 1790 TM,
15 Cytec, Inc., AO-I-2),

(b) Phosphite-type compound (II)

- Tris(2,4-di-*t*-butylphenyl)phosphite (Irgafos 168 TM, Ciba Specialty Chemicals, AO-II-1),
20 - Bis(2,4-dicumylphenyl)pentaerythritol diphosphite (Doverphos S-9228 TM, Dover Chemical Corp., AO-II-2)

(c) Sulphur-containing compound (III)

- Di stearyl-thio-di-propionate (Irganox PS-802, Ciba
25 Specialty Chemicals, AO-III)

Table 1 provides an overview of the concentration of each antioxidant and non-antioxidant additive which are incorporated into the polypropylene homopolymer compositions
30 of Examples 1-10.

After prism extrusion, MFR and YI were determined for each sample. With regard to Examples of Ref. No. 1,3 and 7-10 multiple extrusion at a Brabender extruder were carried out.

Long term heat stability was determined for each sample on pellets at 150°C. When degraded pellets were observed for the first time the YI value was then measured.

- 5 All results of these determinations are summarized in Table 2.

Table 1

Ref. No.	Antioxidant additives						Non-antioxidant additives	
	Phenolic type AO			Phosphite-type AO		Sulphur- containing AO		
	AO-I-1	AO-I-2	AO-I-3	AO-II-1	AO-II-2			
1	1200 ppm	-	-	2400 ppm	-	3000 ppm	600 ppm	2000 ppm
2	1200 ppm	-	-	-	1600 ppm	3000 ppm	600 ppm	2000 ppm
3	1200 ppm	-	-	-	800 ppm	3000 ppm	600 ppm	2000 ppm
4	-	600 ppm	-	1600 ppm	-	3000 ppm	600 ppm	2000 ppm
5	-	300 ppm	-	1600 ppm	-	3000 ppm	600 ppm	2000 ppm
6	-	600 ppm	-	-	800 ppm	3000 ppm	600 ppm	2000 ppm
7	-	300 ppm	-	-	800 ppm	3000 ppm	600 ppm	2000 ppm
8	1200 ppm	-	-	2400 ppm	-	3000 ppm	600 ppm	-
9	1200 ppm	-	-	-	800 ppm	3000 ppm	600 ppm	-
10	-	300 ppm	-	-	800 ppm	3000 ppm	600 ppm	-

Table 2

Ref. No.	mfr after multiple extrusion					YI after multiple extrusion					long term heat stability	
	0.	1.	3.	5.		0.	1.	3.	5.		hours to degrad.	YI after degrad.
1	3,1	3,3	3,7	3,8		-1,4	-1,6	0	1,3		2620	43
2	3,0	-	-	-		-1,5	-	-	-		3070	46
3	3,0	3,2	3,5	3,7		-1,6	-1,1	1,7	3,4		3020	47
4	2,9	-	-	-		-0,8	-	-	-		2500	47
5	3,0	-	-	-		-1,7	-	-	-		2280	35
6	3,0	-	-	-		-1,0	-	-	-		3070	47
7	3,0	3,2	3,6	3,9		-1,7	-0,9	1,7	3		3020	36
8	3,0	3,2	3,6	3,7		-1,9	-1,6	-1,1	0,4		2620	42
9	3,0	3,2	3,5	3,9		-2,2	-2,0	-0,8	0,3		3020	47
10	3,0	3,2	3,8	4,3		-2,4	-1,6	-0,6	0,2		3120	38

Effect of Bis(2,4-dicumylphenyl)pentaerythritol diphosphite
on process stability and LTHS

The equal mfr values after compounding (3,0 +/-0,1) for all
5 of the formulations show a very good process stabilising in
each sample.

In the series of Ref. No. 1-3, Pentaerythrityl-tetrakis(3-
(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate (Irganox
10 1010 TM, AO-I-1) is constant, and 2400 ppm Tris(2,4-di-t-
butylphenyl)phosphite (Irgafos 168 TM, AO-II-1) is compared
with 1600 ppm and 800 ppm of Bis(2,4-dicumylphenyl)-
pentaerythritol diphosphite (Doverphos S-9228 TM) (AO-II-2).
The results of mfr and YI after multiple extrusions are
15 similar, though a little stronger yellowing effect was
observed after the 5th extrusion of the sample comprising 800
ppm Doverphos S-9228 TM (AO-II-2).

Figure 1 shows a comparison of LTHS values (hours at 150°C
before start of degradation) for the formulations with 1200
20 ppm Irganox 1010 TM (AO-I-1). It can be taken from these
results that, in contrast to the generally acknowledged
opinion in the prior art, the phosphite also influences LTHS.
An increase of more than 400 hours at 150° by replacing 2400
ppm Irgafos 168 TM (AO-II-1) with 800 ppm Doverphos S-9228 TM
25 (AO-II-2) is quite considerable. Doubling the amount of
Doverphos S-9228 TM (AO-II-2) only gives a slight increase in
LTHS. This proves that a smaller amount of the preferred
Doverphos S-9228 leads to improved LTHS properties of the
polymer.

30

Figure 2 reflects the corresponding results for samples
comprising another phenolic-type antioxidant, i.e. 1,3,5-
Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-
triazine-2,4,6-(1H,3H,5H)-trione (Cyanox 1790 TM, AO-I-2).

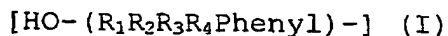
These results show that, by doubling the concentration of Cyanox 1790 TM (AO-I-2) from 300 ppm to 600 ppm, only a slight increase in LTHS was achieved for both Irgafos 168 TM (AO-II-1) and Doverphos S-9228 TM (AO-II-2), but by replacing 1600 ppm Irgafos 168 TM (AO-II-1) with 800 ppm Doverphos S-9228 TM (AO-II-2), the LTHS increased by more than 700 hours (1 month) at 150°C. This finding is surprising in view of the prior art and shows a synergistic effect for the compounds as used.

2000 ppm of the talc Tital 10 TM (Incemin, Inc.) seems to have only a minor or no effect on both process stability and LTHA (Table 2). In this respect, it is to be noted that Tital 10 TM is a very pure talc.

Claims

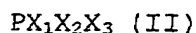
1. A stabilized polymer composition comprising a polymer and an antioxidant composition for improving the long term heat stability of polymers, in particular polyolefins, said antioxidant composition comprising:

(a) 0,01% - 0,5% by weight of at least one sterically hindered phenolic compound, wherein said phenolic compound contains at least one phenolic moiety of general formula (I):



wherein R_1 , R_2 , R_3 or R_4 may be the same or different and at least one of R_1 , R_2 , R_3 or R_4 is selected from the group consisting of branched alkyl having 1 to 12 carbon atoms, preferably tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl, the others of R_1 , R_2 , R_3 or R_4 being H or lower alkyl having 1 to 6 carbon atoms;

(b) 0,01% - 0,5% by weight of at least one phosphorous compound, wherein said phosphorous compound contains at least one phosphorous compound moiety of general formula (II):



wherein X_1 may be R_5 or OR_5 , X_2 may be R_6 or OR_6 , X_3 may be R_7 or OR_7 and R_5 , R_6 or R_7 may be the same or different and at least one of R_5 , R_6 or R_7 is selected from the group consisting of C_1 - C_{25} alkyl group, aryl group or aralkyl group which may be substituted by lower alkyl having 1 to 6 carbon atoms, or two or any of R_5 , R_6 or R_7 may form a ring structure having 4 to 12 carbon atoms,

(c) 0,01% - 1% by weight of at least one sulphur-containing compound of general formula (III):



5 wherein $x = 1$ or 2 , and wherein R_8 and R_9 may be the same or different and are selected from the group consisting of C_{10} - C_{25} alkyl groups optionally being substituted with C_1 - C_{12} alkyl ester carboxylates,
10 wherein said % by weight values are referred to the polymer composition.

2. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition,
15 wherein said antioxidant composition comprises:

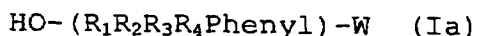
- (a) 0,02% - 0,2% by weight of said at least one sterically hindered phenolic compound,
- (b) 0,03% - 0,2% by weight of said at least one phosphorous compound, and
- 20 (c) 0,05% - 0,6% by weight of said at least one sulphur-containing compound of general formula (III),
wherein said % by weight values are referred to the polymer composition.

25 3. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

- (a) 0,03% - 0,15% by weight of said at least one sterically hindered phenolic compound,
- 30 (b) 0,05% - 0,15% by weight of said at least one phosphorous compound, and
- (c) 0,1% - 0,5% by weight of said at least one sulphur-containing compound of general formula (III),

wherein said % by weight values are referred to the polymer composition.

4. The stabilized polymer composition of any of claims 1 to 3, wherein the phenolic compound contains at least one phenolic moiety of general formula (Ia):



- wherein R_1 and R_4 being in the 2- and 6-position of the phenol residue may be the same or different and are selected from the group consisting of preferably branched C_1 to C_{12} alkyl, particularly tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl residues, R_2 and R_3 having the meaning as given before, and W is selected from C_1 to C_{12} alkyl, C_1 to C_{12} alkoxy, C_1 to C_{12} alkyl carboxylate or C_1 to C_{12} alkyl substituted by another group of the formula $\text{HO}-(\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{Phenyl})-$, wherein R_1 to R_4 have the meaning as indicated before.

5. The stabilized polymer composition of any of claims 1 to 4, wherein the phosphorous compound comprises a phosphite moiety of the formula $\text{Bis}(\text{R}_{10})$ -pentaerythrityldiphosphite, wherein R_{10} is selected from C_1 - C_{25} alkyl group or aryl group which may be substituted by lower alkyl having 1 to 6 carbon atoms.

6. The stabilized polymer composition of any of claims 1 to 5, wherein the sulphur-containing compound of general formula (III):



is selected from Di(C₁-C₂₀) alkyl-(S)_x-di-carboxylate wherein the carboxylic acid is selected from C₁ to C₁₂ alkyl carboxylic acids.

- 5 7. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:
- 2,6-Di-tert.-butyl-4-methyl phenol;
 - Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-
 - 10 hydroxyphenyl)-propionate;
 - Octadecyl 3-(3',5'-di-tert.-butyl-4-
 - hydroxyphenyl)propionate;
 - 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-
 - hydroxyphenyl) benzene;
 - 15 - 2,2'-Thiodiethylene-bis-(3,5-di-tert.-butyl-4-
 - hydroxyphenyl)-propionate;
 - Calcium-(3,5-di-tert.-butyl-4-hydroxy benzyl monoethyl-
 - phosphonate);
 - 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-
 - 20 isocyanurate;
 - Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl) butanoic
 - acid)-glycolester;
 - 4,4'-Thiobis (2-tert.-butyl-5-methylphenol);
 - 2,2'-Methylene-bis(6-(1-methyl-cyclohexyl)para-cresol);
 - 25 - N,N'-hexamethylene bis(3,5-di-tert. Butyl-4-hydroxy-
 - hydrocinnamamide;
 - 2,5,7,8-Tetramethyl-2(4',8',12'-trimethyltridecyl)
 - chroman-6-ol;
 - 2,2'-Ethylidenebis(4,6-di-tert.-butylphenol);
 - 30 - 1,1,3-Tris(2-methyl-4-hydroxy-5-tert.-
 - butylphenyl)butane;
 - 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-
 - 1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;

- 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane;
- 1,6-Hexanediyl-bis(3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene-propanoate);
- 2,6-Di-tert.-butyl-4-nonylphenol;
- 3,5-Di-tert.-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris(2-hydroxyethyl)-s-triazine-2,4,6(1H,3H,5H)-trione;
- 4,4'-Butylidenebis(6-tert. Butyl-3-methylphenol);
- 2,2'-Methylene bis(4-methyl-6-tert.-butylphenol);
- 2,2-Bis(4-(2-(3,5-di-t-butyl-4-hydroxyhydrocinnamoyloxy)ethoxyphenyl))propane;
- Triethyleneglycol-bis-(3-tert.-butyl-4-hydroxy-5-methylphenyl) propionate;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, C₁₃-C₁₅-branched and linear alkyl esters;
- 6,6'-Di-tert.-butyl-2,2'-thiodi-p-cresol;
- Diethyl((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl) phosphonate;
- 4,6-Bis(octylthiomethyl)o-cresol;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, C₇-C₉-branched and linear alkyl esters;
- 1,1,3-Tris[2-methyl-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-5-t-butylphenyl] butane; and
- Butylated reaction product of p-cresol and dicyclopentadiene.

8. The stabilized polymer composition of any of the precedent claims, wherein the phosphorous compound is selected from the group consisting of:

- Tris(2,4-di-t-butylphenyl) phosphite;

- Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite
 - Bis (2,4-di-t-butylphenyl)-pentaerythrityl-di-phosphite;
- 5 - Di-stearyl-pentaerythrityl-di-phosphite;
- Tris-nonylphenyl phosphite;
- Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
- 2,2'-Methylenebis (4,6-di-t-butylphenyl) octyl-
- 10 phosphite;
- 1,1,3-Tris (2-methyl-4-ditridecyl phosphite-5-t-butylphenyl) butane;
- 4,4'-Butylidenebis (3-methyl-6-t-butylphenyl-di-tridecyl) phosphite;
- 15 - Bis(2,4-dicumylphenyl)pentaerythritol diphosphite;
- Bis(2-methyl-4,6-bis(1,1-dimethylethyl)phenyl)phosphorous acid ethylester;
- 2,2',2''-Nitrilo triethyl-tris(3,3',5,5'-tetra-t-butyl-1,1'-biphenyl-2,2'-diyl)phosphite);
- 20 - Phosphorous acid, cyclic butylethyl propandiol, 2,4,6-tri-t-butylphenyl ester; Bis (2,4,6-tri-t-butylphenyl)-pentaerythrityl-di-phosphite;
- 2,2'-Ethylidenebis (4,6-di-t-butylphenyl) fluorophosphonite
- 25 - 6- (3-tert-Butyl-4-hydroxy-5-methylphenyl) propoxy)-2,4,8,10-tetra-tert. butyldibenz (d,t) (1.3.2) dioxaphosphopin; and
- Tetrakis-(2,4-di-t-butyl-5-methyl-phenyl)-4,4'-biphenylen-di-phosphonite.

30

9. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is selected from the group consisting of:

- Di-stearyl-thio-di-propionate;
- Di-palmityl/stearyl-thio-di-propionate;
- Di-lauryl-thio-di-propionate;
- Di-tridecyl-thio-di-propionate;
- 5 - Di-myristyl-thio-di-propionate;
- Pentaerythritol octyl thiodipropionate;
- Lauryl-stearyl-thio-di-propionate;
- Di-octadecyl-disulphide;
- Di-tert-dodecyl-disulphide and
- 10 - Pentaerythritol-tetrakis-(3-laurylthiopropionate)

10. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:

- 15 - Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;
- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
- 20 - 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-isocyanurate;
- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl)butanoic acid)-glycolester; and
- 25 - 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane.

11. The stabilized polymer composition of any of the preceding claims, wherein the phosphite compound is selected from the group consisting of:

- 30 - Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite;

- Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
 - Di-stearyl-pentaerythrityl-di-phosphite; and
 - Bis(2,4-dicumylphenyl)pentaerythritol diphosphite.

5

12. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is Di-stearyl-thio-di-propionate or Di-tert-dodecyl-disulphide.

10

13. The stabilized polymer composition of any of any of the preceding claims, wherein

(a) the sterically hindered phenolic compound is 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione or pentaerythrityl-

15 tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;

(b) the phosphite compound is bis(2,4-dicumylphenyl)pentaerythritol diphosphite; and

(c) the sulphur-containing compound is Di-stearyl-thio-di-propionate.

20

14. The stabilized polymer composition of any of claims 1-13, wherein said composition further comprises metal deactivators and/or UV-stabilisers.

25

15. The stabilized polymer composition of claim 14, wherein said UV-stabilizers are sterically hindered amines.

30

16. The stabilized polymer composition of any of claims 1-16 wherein said polymer is selected from the group consisting of polyolefins, polyethers, polyimides, polyamides and polyesters or mixtures thereof.

17. The stabilized polymer composition of claim 16, wherein said at least one polymer is a homo- or co-polymer of polyethylene, polypropylene and polybutadiene.

5 18. Use of the antioxidant composition as defined in any of claims 1-14 for reducing degradation of a polymeric material during processing and end use of said polymeric material.

10 19. The use of claim 18 for increasing long term thermal stability of the polymeric material.

20. Method for producing a polymeric article having an improved long term thermal stability against ageing by
15 radical degradation processes comprising the steps of:
 (a) providing an unstabilised base polymer material;
 (b) adding to said base polymer material the antioxidant composition as defined in any of the preceding claims;
 (c) converting the composition obtained in step (b) in a
20 melt-forming process; and
 (d) confectioning the polymeric material obtained in step (c).

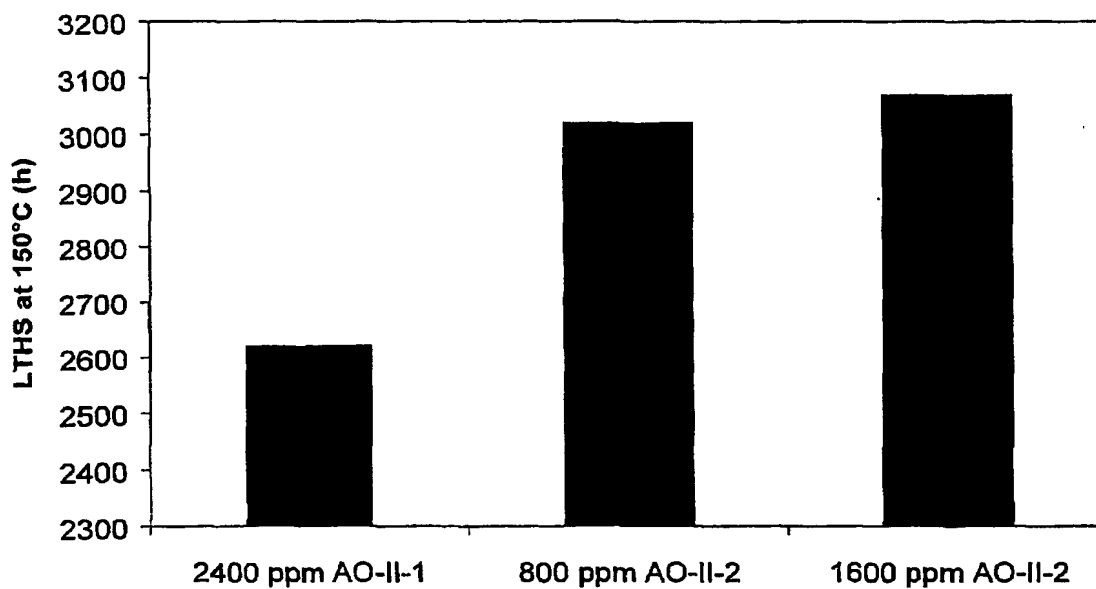
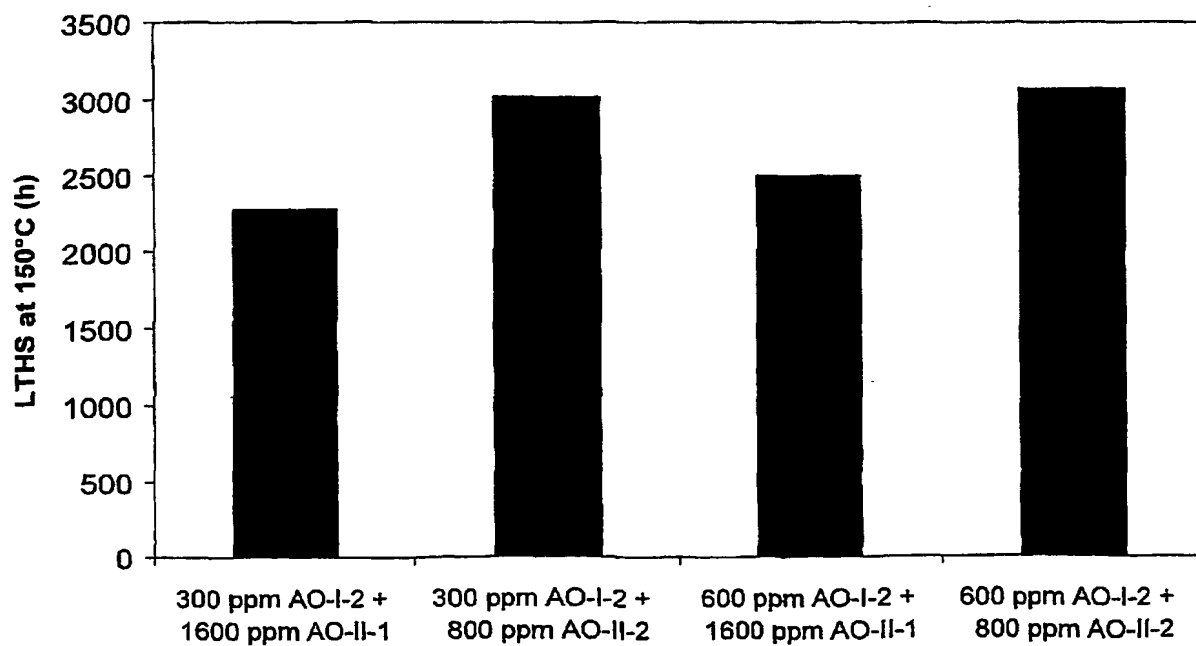
21. The method of claim 19 further comprising adding
25 other stabilisers and/or modifiers before the converting step c).

22. The method of any of claims 20 or 21, wherein the converting step includes injection moulding, blow moulding,
30 rotational moulding and extrusion.

23. The method of any of claims 20 to 22, wherein the confectioning step includes cutting, lamination and/or welding.

24. Polymeric article having an increased long term ageing stability obtained by the method of any of claims 20-23.

5

Figure 1Figure 2

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 02/11258

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/00 //(C08K5/00, 5:13, 5:527, 5:372)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 200138 Derwent Publications Ltd., London, GB; Class A17, AN 2001-365817 XP002243985 & RU 2 166 217 C (REAL SERVICE CABLE CORP) , 27 April 2001 (2001-04-27) abstract	1-4, 6-10, 12, 14, 16, 18
X	EP 0 330 256 A (ENICHEM SINTESI) 30 August 1989 (1989-08-30) examples claims 1, 4, 5, 8, 9	1-10, 14-18
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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'&' document member of the same patent family

Date of the actual completion of the international search

11 June 2003

Date of mailing of the international search report

24/06/2003

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/11258

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 227 948 A (BORG WARNER CHEMICALS INC) 8 July 1987 (1987-07-08) claims 1-17 ---	1-3,5,6, 8,9,12, 14,16-18
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Form PCT/ISA/210 (continuation of second sheet) (July 1982)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/11258

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